

(12) **UK Patent Application** (19) **GB** (11) **2 226 066** (13) **A**
(43) Date of A publication 20.06.1990

(21) Application No 8926613.4

(22) Date of filing 24.11.1989

(30) Priority data

(31) 15395

(32) 25.11.1988

(33) FR

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(51) INT CL^a

E21B 33/138

(52) UK CL (Edition K)

E1F FPC

C3P PHZ

C3W W224 W225

(56) Documents cited

None

(58) Field of search

UK CL (Edition J) C3P PHZ, E1F FPC

INT CL^a C08F, E21B

WPI

(54) Delayed-gelling compositions and their use for plugging subterranean formations

(57) The gelling of vinyl monomers in an aqueous medium in the presence of an organic peroxide polymerization initiator is delayed by employing an inhibitor consisting of an N-nitrosophenyl hydroxyl amine salt in combination with an aminocarboxylic acid. Such compositions are useful for plugging circulation losses in drilling at great depth.

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DELAYED-GELLING COMPOSITIONS CONTAINING
UNSATURATED MONOMERS AND THEIR USE FOR PLUGGING
CIRCULATION LOSSES IN BORE HOLES

5 The present invention relates to delayed-gelling compositions containing unsaturated monomers and to the use of such compositions in the treatment of subterranean formations, especially for plugging circulation losses in oil drilling operations, particularly at elevated temperature.

10 During drilling operations in oil or gas deposits, crossing permeable or fractured regions can cause a partial or even total loss of drilling mud.

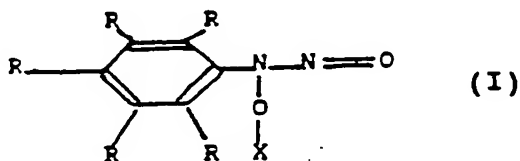
 For reasons of economy (cost of drilling mud) and of safety (stability of the work) it is absolutely necessary to
15 carry out prompt plugging of the circulation losses. It is known to use grouts of water-soluble monomers (acrylamide, methylolacrylamide, other acrylic and methacrylic derivatives, etc) which, when suitably formulated (e.g. with
catalysts, weighting materials, viscosity modifiers,
20 retardants), polymerize to a (hydro) gel of three-dimensional structure which is insoluble in water but capable of swelling in contact with it.

 These grouts are generally employed

satisfactorily for drilling operations at depths
corresponding to a temperature of the order of 0 to 60°C;
however, the use of these grouts at greater depths does not
generally make it possible to work for more than 10 hours
5 because the temperature rise, which is a function of the
depth, causes a substantial shortening of the setting time.

It is known to stabilize vinyl monomers using
N-nitrosophenylhydroxylamine salts (US Patents Nos. 2,758,131
and 2,773,874, German Patent No. 1,239,679). It has been
10 found that such inhibitors are not sufficiently effective at
elevated temperature, especially above 80°C.

The present invention provides compositions
containing unsaturated monomers capable of forming hydrogels
in an aqueous medium in which gelling is delayed. These
15 compositions comprise, in addition to water and at least one
said monomer, a polymerization initiator in the form of a
water-soluble or water-dispersible organic peroxide having a
half-life of at least 10 hours at 60°C, and a polymerization
inhibitor consisting of an alkali metal or ammonium salt of
20 N-nitrosophenylhydroxylamine of formula:



where at least two of the radicals R denote hydrogen, and the other radicals R are the same or different and each denotes methyl, methoxy, ethoxy, nitro, amino, hydroxyl or chloro, X is an ammonium group or an alkali metal cation, the said salt
5 being used in combination with an aminocarboxylic acid in acidic or basic form.

The unsaturated monomers employed are those capable of forming a hydrogel by polymerization in an aqueous medium; they are preferably acrylic monomers.

10 Among the acrylic monomers capable of forming a hydrogel by polymerization in an aqueous medium there may be mentioned water-soluble or water-dispersible acrylic monomers of the acrylic or methacrylic acid type, acrylamide, N-alkyl-acrylamides containing a C₁-C₄ alkyl radical,
15 methylolacrylamide, methylolmethacrylamide, C₁-C₄ alkyl acrylates, inorganic (meth)acrylates, etc, if necessary and at least preferably mixed with at least one water-soluble or dispersible, ethylenically di- or polyunsaturated crosslinking monomer of the type of methylenetriacrylamide,
20 methylenebismethacrylamide, 1,2-dihydroxyethylenebisacrylamide, 1,2-dihydroxyethylenebismethacrylamide, N-methylol-1,2-dihydroxyethylenebisacrylamide, 1,3-bis(acrylamidomethyl)-1,2-imidazolidone, 1,3-bis(methacrylamidomethyl)-2-imidazolidone and allyl methacrylate.

25 The ethylenically di- or polyunsaturated crosslinking acrylic monomers at least preferably present may

represent up to approximately 5% of the total weight of the acrylic monomers.

tert-Butyl, tert-amyl and cumene hydroperoxide, etc, may be preferably mentioned among the organic peroxide
5 initiators which can be employed.

The ammonium salt of N-nitrosophenylhydroxylamine, commonly called "cupferron", may be mentioned more particularly among the salts capable of forming the inhibitor; others which can be reported are the ammonium
10 salts of N-nitroso-4-methylphenylhydroxylamine, of N-nitroso-2,6-dinitrophenylhydroxylamine, of N-nitroso-2-hydroxy-4-chlorophenylhydroxylamine, of N-nitroso-2,6-dinitro-4-chlorophenylhydroxylamine, of N-nitroso-2-methoxy-4-aminophenylhydroxylamine,
15 of N-nitroso-3-ethoxyphenylhydroxylamine, etc.

Among the aminocarboxylic acids which can be employed there may be mentioned:

- ethylenediaminetetracetic acid (EDTA)
- diethylenetriaminopentacetic acid (DTPA)
- 20 ⇒ - nitrilotriacetic acid (NTA)
- ⇒ - N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA)
- diaminopropanoltetracetic acid (DPTA)
- N,N-di(2-hydroxyethyl)glycine (DHEG)

25 in the form of acid or preferably of their alkali metal, in particular sodium, salts.

The following may be employed to implement

the invention:

- from 0.2 to 3%, preferably from 0.5 to 2%, by weight of initiator relative to the weight of monomers,
 - from 0.03 to 0.8%, preferably from 0.05 to 0.5%, by
5 volume of N-nitrosophenylhydroxylamine salt (or one of its derivatives) relative to the volume of monomers, and
 - from 0.03 to 8%, preferably from 0.05 to 5% by volume of aminocarboxylic acid relative to the volume of monomers.
- Such compositions preferably comprise from 1 to 60 parts by
10 volume, preferably from 10 to 30 parts by volume, of at least one unsaturated monomer capable of forming a hydrogel, the complement to 100 parts by volume being water.

Fluid systems incorporating the compositions of the invention exhibit a setting time longer than 10 hours at 60°C
15 and generally longer than 15 hours at 80°C. The setting time means the time interval between the instant when the various constituents of the fluid system are mixed and the instant when the product no longer flows.

Conventional additives may be incorporated in the
20 compositions of the invention, making it possible to adjust particularly their density and their viscosity to the values required by the depth and the state of the drilling operation (e.g. gravity fillers of the barium sulphate type, various reinforcing or extending fillers of the bentonite or
25 pyrogenic silica type, and various thickeners of the xanthan gum type).

Because of their increased setting time at high temperature, these compositions may be employed for plugging circulation losses in drilling at great depth, for oil or otherwise, when crossing highly permeable or fractured regions. They can be applied equally well in an aquifer medium (fresh water) and in a saline medium (seawater, salt water, saturated salt water).

The following Examples illustrate the invention.

Examples 1 to 44

10 Preparation of delayed-gelling compositions
in fresh water

50 cm³ of a mixture comprising the following are homogenized for 5 minutes:

- dilution water (tap water)
- 15 - an aqueous solution (in tap water) at a concentration of 1% by volume of a commercial aqueous solution containing 70% by volume of tert-butyl or tert-amyl hydroperoxide (TBHP or TAHP); the commercial aqueous solutions containing 70% by volume of TBHP or of TAHP are marketed by the Société
- 20 Chalonnaise de Peroxydes Organiques and have densities of the order of 0.94 g/cm³ and 0.9 g/cm³ at 20°C respectively.
- an aqueous solution (tap water) containing 1% by volume of cupferron,
- an aqueous solution (tap water) containing 0.1%, 1% or 10% by volume of EDTA sodium salt or of DTPA sodium salt.

Into this mixture are incorporated 50 cm³ of a commercial aqueous solution of Rocagil BT (methyrolacrylamide-based solution marketed by Rhône-Poulenc at a concentration of approximately 40% by volume).

The whole is heated to the chosen temperature for measuring the setting time (85°C or 94°C, depending on the examples).

The setting time is defined as being the period separating the time when the whole is heated to the chosen temperature and the time when the gel has formed.

The quantities of the various components employed and the results obtained appear in Tables I to VII.

Examples 1 to 5 are given by way of comparison.

Examples 45 to 53

Preparation of delayed-gelling compositions in seawater.

The operating procedure is the same, but the components are:

- synthetic seawater containing 34 g/l of salts, as dilution water,
- solutions of TBHP, of EDTA or DTPA sodium

salt and of cupferron in synthetic seawater, and

- the same solution of Rocagil BT (fresh water).

The quantities of the various components employed and the results obtained appear in Table VIII.

5 Examples 54 to 59

Preparation of delayed-gelling compositions in
saturated salt water

The operating procedure is the same, but the components are:

- 10 - saturated salt water containing 357 g/l of sodium chloride, as a dilution water,

- solutions of TBHP and of EDTA sodium salt in saturated salt water,

- 15 - a solution containing 1% by volume of cupferron in tap water, and

- the same solution of Rocagil BT (fresh water).

The quantities of the various components employed and the results obtained appear in Table IX.

In Tables I to IX

- 20 () 40% means volume of aqueous solution containing 40% by volume

- () 0.1% means volume of aqueous solution containing 0.1% by volume

- 25 () % means volume of aqueous solution containing 1% by volume

()10% means volume of aqueous solution containing
10% by volume
[] means volume of active substance in the
said solution.

5 In the case of the TBHP or TAHP initiator

()1% means volume of aqueous solution containing
1% by volume of commercial aqueous solution
containing 70% by volume
[] means volume of commercial aqueous solution
10 containing 70% by volume

EDTA or EDTA+ means EDTA sodium salt

DTPA or DTPA++ means DTPA sodium salt.

Table 1

Examples	1	2	3	4	5
BT (cm ³) () 40 %	50	50	50	50	50
[]	20	20	20	20	20
TBHP (cm ³) () 1 %	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 %	1		0.1	0.5	0.8
[]	0.01	0	0.001	0.005	0.008
EDTA (cm ³) () 1 %		20	0.1	0.5	0.8
[]	0	0.2	0.001	0.005	0.008
water (cm ³)	39	20	39.8	39	38.4
setting time (min) at 85°C	95	40	20	110	180

Table 2

Examples	6	7	8	9	10	11	12	13
BT (cm ³) () 40 ±	50	50	50	50	50	50	50	50
[]	20	20	20	20	20	20	20	20
TBHP (cm ³) () 1 ±	10	10	10	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 ±	2	2	2	2	2	2	2	2
[]	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
EDTA (cm ³) () 1 ±	2	10	20	30				
() 10 ±					4	5	6	10
[]	0.02	0.1	0.2	0.3	0.4	0.5	0.6	1
water (cm ³)	36	28	18	8	34	33	32	28
setting time (min) at 85°C	950	1200	1290	1415	1500	1655	1840	2120

Table 3

Examples	14	15	16	17	18	19	20
BT (cm ³) () 40 ±	50	50	50	50	50	50	50
[]	20	20	20	20	20	20	20
TBHP (cm ³) () 1 ±	10	10	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERON (cm ³) () 1 ±	1	5	9	1	3	5	10
[]	0.01	0.05	0.09	0.01	0.03	0.05	0.1
EDTA (cm ³) () 0.1 ±		10	10				
[]	1			5	5	5	5
	0.01	0.01	0.01	0.05	0.05	0.05	0.05
water (cm ³)	38	25	21	34	32	30	25
setting time (min) at 85°C	770	1100	1130	960	1220	1280	1160

Table 4

Examples	21	22	23	24	25	26	27
BT (cm ³) () 40 %	50	50	50	50	50	50	50
[]	20	20	20	20	20	20	20
TBHP (cm ³) () 1 %	10	10	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 %	1	3	5	10	1	3	5
[]	0.01	0.03	0.05	0.1	0.01	0.03	0.05
EDTA (cm ³) () 1 %	10	10	10	10			
() 10 %	0.1	0.1	0.1	0.1	6	6	6
[]					0.6	0.6	0.6
water (cm ³)	29	27	25	20	33	31	29
setting time (min) at 85°C	785	1250	1405	1120	1420	1960	3600*

* : soft gel

Table 5

Examples	28	29	30
BT (cm ³) () 40 %	50	50	50
[]	20	20	20
TBHP (cm ³) () 1 %	10	10	30
[]	0.1	0.1	0.3
CUPFERRON (cm ³) () 1 %	2	2	2
[]	0.02	0.02	0.02
EDTA (cm ³) () 1 %	15	20	10
[]	0.15	0.2	0.1
water (cm ³)	23	18	8
setting time (min).			600
at 85°C			
at 94°C	620	710	

▪ : soft gel

Table 6

Examples	31	32	33	34	35	36
BT (cm ³) () 40	50	50	50	50	50	50
[]	20	20	20	20	20	20
TAHP (cm ³) () 1	10	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1	2	2	2	2	2	2
[]	0.02	0.02	0.02	0.02	0.02	0.02
EDTA (cm ³) () 1	5	10	20			
() 10				4	5	6
[]	0.05	0.1	0.2	0.4	0.5	0.6
water (cm ³)	33	28	18	34	33	32
setting time (min) at 85°C	850	1030	1200	1490	1520	1800

Table 7

Examples	37	38	39	40	41	42	43	44
BT (cm ³) () 40 ±	50	50	50	50	50	50	50	50
[]	20	20	20	20	20	20	20	20
TAMP (cm ³) () 1 ±	10	10	10	10	10	10	10	10
[]	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 ±	2	2	2	2	2	3	3	3
[]	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03
DTPA (cm ³) () 1 ±	5	20	30			5	20	30
() 10 ±				5	10			
[]	0.05	0.2	0.3	0.5	1	0.05	0.2	0.3
water (cm ³)	33	18	8	33	28	32	17	7
setting time at 85°C	1110	1600	2300	3100	5400*	1100	1750	2500

* : very soft gel

Table 8

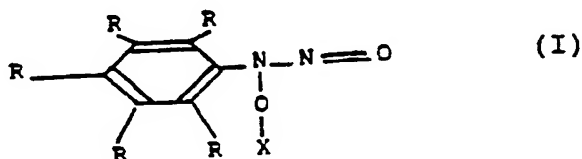
Examples	45	46	47	48	49	50	51	52	53
BT (cm ³) () 40 ±	50	50	50	50	50	50	50	50	50
()	20	20	20	20	20	20	20	20	20
TBHP (cm ³) () 1 ±	10	10	10	10	10	10	10	10	10
()	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 ±	2	2	2	2	2	2	2	2	2
()	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
EDTA+ (cm ³) ₃ () 1 ±	+ 10	+ 30		+ 5	+ 10	+ 20	+ 30		
DTPA ++ (cm ³) () 10 ±			+ 5					++ 5	++ 10
()	+ 0.1	+ 0.3	+ 0.5	+ 0.05	+ 0.1	+ 0.2	+ 0.3	+ 0.5	+ 1
water (cm ³)	28	8	33	33	28	18	8	33	28
setting time at 85°C	1650	1800	1900	1580	1680	2100	2300	2960	3010

Table 9

Examples	54	55	56	57	58	59
BT (cm ³) () 40 %	50	50	50	50	50	50
()	20	20	20	20	20	20
TBHP (cm ³) () 1 %	10	10	10	10	10	10
()	0.1	0.1	0.1	0.1	0.1	0.1
CUPFERRON (cm ³) () 1 %	2	2	2	2	2	2
()	0.02	0.02	0.02	0.02	0.02	0.02
EDTA (cm ³) () 1 %	5	10	20	30		
() 10 %					5	10
()	0.05	0.1	0.2	0.3	0.5	1
water (cm ³)	33	28	18	8	33	28
setting time at 85°C	950	1250	1340	1580	1820	2900

CLAIMS

1. An aqueous composition comprising at least one unsaturated monomer capable of forming a hydrogel, a polymerization initiator in the form of a water-soluble or water-dispersible organic peroxide having a half-life of at least 10 hours at 60°C, and a polymerization inhibitor consisting of an alkali metal or ammonium salt of an N-nitrosophenylhydroxylamine of formula:



- where at least two of the radicals R denote hydrogen, and the other radicals R are the same or different and each denotes methyl, methoxy, ethoxy, nitro, amino, hydroxyl or chloro, X is an ammonium group or an alkali metal cation, the said salt being used in combination with an aminocarboxylic acid in acidic or basic form.

2. A composition according to claim 1, comprising
- from 1 to 60 parts by volume of the said monomer(s),
 - from 0.2 to 3% by weight of initiator relative to the weight of monomer(s),
 - from 0.03 to 0.8% by volume of N-nitrosophenylhydroxylamine salt (or one of its derivatives) relative to the volume of monomers,

- from 0.03 to 8% by volume of aminocarboxylic acid relative to the volume of monomers, and

- the complement to 100 parts by volume of water.

3. A composition according to claim 2, comprising

5 - from 10 to 30 parts by volume of the monomer,

- from 0.5 to 2% by weight of initiator relative to the weight of monomers,

- from 0.05 to 0.5% by volume of N-nitrosophenylhydroxylamine salt (or one of its derivatives) relative to
10 the volume of monomers,

- from 0.05 to 5% by volume of aminocarboxylic acid relative to the volume of monomers, and

- the complement to 100 parts by volume of water.

4. A composition according to any one of claims 1 to 3,
15 in which the unsaturated monomers capable of forming a hydrogel are acrylic monomers.

5. A composition according to any one of claims 1 to 4, in which the initiator is tert-butyl hydroperoxide, tert-amyl hydroperoxide or cumene hydroperoxide.

20 6. A composition according to any one of claims 1 to 5, in which the polymerization inhibitor is the ammonium salt of N-nitrosophenylhydroxylamine (cupferron) used in combination with an aminocarboxylic acid in acidic or basic form.

7. A composition according to claim 7, in which the
25 aminocarboxylic acid in basic form is an alkali metal salt of ethylenediaminetetracetic acid or of

diethylenetriaminopentacetic acid.

8. A composition according to claim 1 substantially as described in any one of the foregoing Examples 6 to 59.

9. A method of preventing or reducing circulation losses
5 in bore holes which comprises plugging said losses with a composition as claimed in any one of claims 1 to 8.